Stretched Exponential Relaxation on the Hypercube and the Glass Transition

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We study random walks on the dilute hypercube using an exact enumeration Master equation technique, which is much more efficient than Monte Carlo methods for this problem. For each dilution p the form of the relaxation of the memory function $q(t)$ can be accurately parametrized by a stretched exponential $q(t) = \exp(-(t/\tau)^{\beta})$ over several orders of magnitude in $q(t)$. As the critical dilution for percolation p_c is approached, the time constant $\tau(p)$ tends to diverge and the stretching exponent $\beta(p)$ drops towards 1/3. As the same pattern of relaxation is observed in wide class of glass formers, the fractal like morphology of the giant cluster in the dilute hypercube is a good representation of the coarse grained phase space in these systems. For these glass formers the glass transition can be pictured as a percolation transition in phase space.

Complex systems generally show strongly non-exponential dynamics. In 1854 R.Kohlrausch used a phenomenological expression $q(t) = C\exp(-(t/\tau)^{\beta})$ to parametrize polarization decay data in Leiden jars [1]. Rediscovered more than a century later, again in the context of dielectric relaxation [2], this "stretched exponential" or KWW expression has become ubiquitous in phenomenological analyses of relaxation data, experimental or numerical [3]. Analytical arguments have been given as to why certain hierarchical or trap model systems show KWW relaxation [4,5], but there has always been a school of thought which considers that in the context of real glasses this expression is nothing more than a convenient fitting function of no fundamental significance.

An alternative mechanism for KWW relaxation can be provided by a complex closed space approach. For random walks on a high dimensional critical percolation cluster in Euclidean space [6], it is known that $\langle r^2 \rangle \propto t^{1/3}$. It was conjectured [7] that random walks on a dilute hypercube in high dimension would necessarily lead to stretched exponential relaxation with a limiting value of $\beta = 1/3$ at percolation. Here we use an exact enumeration Master equation method which provides results of high precision for this problem. We find that the KWW functional form accurately fits data extending over a very wide range of $q(t)$ values (from about 0.5 to 10^{-5}), and that β tends to 1/3 at percolation, as predicted. These results demonstrate that in the context of glassy systems the stretched exponential is not just an empirical fitting function, but that it has a precise mathematical and physical significance. A predictive generic picture for the glass transition can be obtained by identifying the glass transition with a percolation transition in phase space.

Imagine a hypercube in high dimension N with a fraction p of its sites occupied at random. Clusters are defined as sets of occupied sites having one or more occupied sites as neighbors. It has been proved mathematically [8] that there is a critical "percolation" concentration p_c given by

$$p_c = \sigma + \frac{3}{2}\sigma^2 + \frac{15}{14}\sigma^3 + \dots \tag{1}$$

Where $\sigma = 1/(N-1)$. For $p > p_c$ there exists a giant spanning cluster while for $p < p_c$ there exist only small clusters with less than N elements.

Now consider the relaxation due to random walks on the giant cluster of sites, a strictly mathematical problem which apparently has not been solved analytically. For a given realisation of the partially occupied hypercube with $p > p_c$ we can define a random walk among sites on the giant cluster. The walker starts at any such site i_o. A site j near neighbor to i_o is drawn at random. If j is on the giant cluster (and so "allowed") the walker moves to j. Otherwise the draw is repeated until an allowed site is found. Each draw, successful or not, is considered one time step. The procedure is iterated.

We identify the distance H_{ik} between sites i and k on the hypercube with the Hamming distance, which is just the minimal number of moves needed to go from i to k on the full hypercube. The value of the normalized memory function $q_n(t)$ after time t for a given walk n starting from i_o and arriving at k_n after time t can be defined by $(2H_{ik_n(t)} - N)/(2N)$. The definition is identical to that of the autocorrelation function relaxation for the N Ising spins. The value averaged over many walks will go to zero at long t.

Relaxation in the dilute hypercube has already been studied numerically by Monte Carlo techniques [9,10]. In the brute force Monte Carlo approach taking a mean over independent walks, the statistical noise becomes important at long t, limiting accuracy [10]. The exact enumeration considers a Master equation to study the time evolution of the entire probability distribution for the walker after t steps, $\vec{\rho(t)}$, which we will call the state vector. Each vertex of the hypercube is associated to an integer $0 \le i \le 2^N - 1$. At $t = 0$ the walker is localized on a single summit i_o on the hypercube; the probability distribution then diffuses over the system at each time step following the equation:

$$\begin{aligned}\rho_i(t) &= \rho_i(t-1) \\ &+ \left[\sum_j \rho_i(t-1)W(j \to i) - \rho_j(t-1)W(i \to j)\right]\end{aligned} \tag{2}$$

where $W(i \to j)$ represents the transition probability that is given by:

$$W(i \to j) = \begin{cases} \frac{1}{N} & \text{if } i \text{ and } j \text{ are allowed first neighbours} \\ 0 & \text{otherwise} \end{cases} \tag{3}$$

Equation 2 can be rephrased as:

$$\vec{\rho}(t) = F\vec{\rho}(t-1) \tag{4}$$

where F is the linear evolution operator. Our numerical algorithm catalogues all sites on the giant cluster for each particular realization of the hypercube, and then equation (2) is iterated for one particular starting point. Close to p_c where time scales are long and there are fewer sites, it is more efficient to diagonalize the evolution operator F.

By explicitly solving the master equation we obtain exact results (to within numerical rounding errors) for each combination of one realization of the hypercube occupation, and one given starting point on the giant cluster. There is no statistical "noise", and by averaging over a moderate number of independent samples a mean $q(t)$ curve can be obtained, lying very close to the infinite ensemble average even to long times.

In practice calculations were done on dimension $N = 16$ for values of p from 0.5 to 0.073 (which is close to p_c). At least 100 samples were used at each p. N must be large; the present value was limited by computer memory considerations.

We expect three relaxation regimes *a priori*. At short times $q(t)$ will behave as $1-\alpha t$ where α is the probability that a step will be made at a given attempt. Short time decay will thus be $\exp(-\alpha t)$. For very long t finite size effects will set in (the number of sites is finite for finite N) and a second crossover back to exponential relaxation will occur. Between these two limiting regimes, as the system explores the labyrinthine geometry of the giant cluster there will be the slow relaxation regime which interests us.

The numerical data obtained together with the stretched exponential fits are shown as $\log q(t)$ against $\log(t)$ in Figure (1). The normalization parameter C is always close to 1. It can be seen immediately that the fits are of excellent quality and that they extend down to $q(t)$ values as low as 10^{-5}.

There are various methods of exhibiting this sort of data in order to make stringent tests of the functional form of $q(t)$. For example, Figure (2) shows $\log[-\log q(t)]$ against $\log(t)$. In this plot perfect pure or stretched exponentials should be straight lines at long t, with the pure exponential having slope one. Over a very wide intermediate time regime, at each p the functional form of $q(t)$ is indistinguishable from a stretched exponential. As p approaches p_c the time scale τ tends to diverge and the stretching exponent β tends to near 1/3. The results strongly confirm the earlier conjectures and numerical work [7,9–11].

In all relaxation models including the present one the shape of the decay can be related formally to a particular distribution of relaxation times of independent modes of the system. In trap models which have been studied intensively [3,5,12] individual non-interacting walkers fall into random traps, giving stretched exponential decay of the number of surviving walkers in the appropriate limits. The present model is not in the class of models with spins relaxing independently at different rates, and the initial site is not a privileged configuration. All the relaxations of the single spins are coupled together implicitly through the complex morphology of the giant cluster. As the spins are strongly interacting, it is essential not to confuse the *modes* with the individual elements (spins) which are relaxing. Thus for the present calculations the effective number of spins is small ($N = 16$) but the number of independent modes is much bigger: it is equal to the number of eigenstates of F, i.e. to $p2^N$, typically of the order of 10^4 modes for $N = 16$. The mode spectrum is discrete and by definition has upper and lower limits. For times less than the minimum characteristic time, relaxation will be exponential, and for times much longer than the (N and p dependent) maximum characteristic time there must again be a second exponential regime, the finite size limit discussed above. The short time regime can be seen on all the curves, for $q(t)$ values above about 0.5; the begining of the long time tendency to exponential decay is only visible for the lowest values of p where the number of modes is smaller and where the calculations have been taken to very long t. If calculations could be carried out for much larger N the ultimate exponential regime would only appear at extremely long times and small $q(t)$.

In a sense the present model expresses concretely the physical picture proposed by Palmer et al [4] where the relaxation of each element depends on its instantaneous environment, but in contrast to [4] the mode relaxation time distribution is not injected "by hand" but emerges naturally as a consequence of the fractal-like closed space morphology of the giant cluster, with no adjustable parameters of any kind. It is important that the present approach not only leads necessarily to the stretched exponential functional form, but provides an explicit quantitative relation between the time scale and the stretching. As p drops towards p_c the time scale $\tau(p)$ gets progressively longer (a divergence at p_c in the very large N limit). Concomitantly $\beta(p)$ decreases from 1 at large p towards a limit of 1/3 at p_c, (figure (3)). Both effects reflect the increasing sparseness and complexity of the giant cluster with decreasing p. The limiting value of 1/3 for β when τ diverges is a consequence of the "percolation fractal" morphology of the sparse giant cluster [7].

We can now compare heuristically the model data with examples of numerical and experimental relaxation results. The autocorrelation function relaxation in the 3d bimodal Ising spin glasses has been studied numerically to high precision [13]. The long time relaxation function above the ordering temperature is of stretched exponential form with an exponent β which tends to 1/3 within numerical accuracy at the temperature at which the times scale τ diverges. Relaxation in other spin glasses are of the same limiting form, independently of space dimension or of the type of spin-spin interaction [14]. This pattern of behaviour is not restricted to spin glasses. For instance the relaxation of a colloid glass former [15], a system having an entirely different microscopic mechanism for glassyness, again shows stretched exponential decay with β tending to 1/3 as τ diverges with concentration because of steric hindrance. A large number of polymer glass formers also show a similar characteristic relaxation pattern [16].

What is the logical connection between the dilute hypercube random walk and relaxation in glasses ? The ensemble of all possible configurations of a thermodynamic system form a high dimensional closed space. The *available* phase space at temperature T can be considered at the microcanonical level as the set of configurations having the appropriate energy for that temperature,

$E(T)$. This available phase space becomes sparser as T decreases. Phase transitions correspond to discrete qualitative changes in the morphology of the available phase space with temperature; thus at a standard ferromagnetic second order transition T_c the phase space splits into two. Also quite generally, relaxation is just the consequence of the random walk of the configuration point of the whole system in the available phase space, and its form is necessarily a reflection of the morphology of this phase space. Explicitly the N dimension hypercube is exactly the total phase space of an N spin Ising model; the spin by spin relaxation of a coupled N spin Ising system can be mapped directly onto a random walk of the configuration point on the thermodynamically available sites of the N dimension hypercube [13]. For systems with more complicated total phase spaces than the hypercube, the same argument applies *mutatis mutandi*.

A non-exponential relaxation means a complex phase space; the striking ressemblence between the dilute hypercube relaxation pattern and the relaxation observed in the numerical spin glasses or experimental glasses we have cited necessarily implies similarities at the level of phase space geometry. Thus, at short times (fine grained phase space) the relaxation will depend on the details of the physics of each system, but at moderate and long times (coarse grained phase space) these systems all appear to have the same specific percolation-fractal-like phase space morphology with its characteristic relaxation signature, the precursor of a phase space percolation breakdown at the glass transition. By continuity, below the percolation transition the phase space would split into many inequivalent clusters, meaning for the thermodynamic systems a transition to a frozen glassy state. The glass transition corresponding to this description is a continuous transition, but in an entirely different class from standard second order transitions.

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FIGURE CAPTIONS

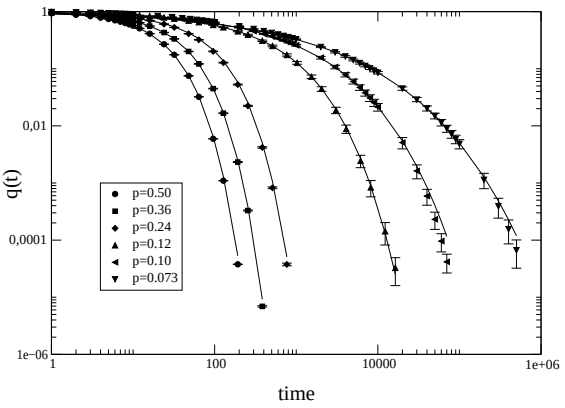

FIG. 1. Decay of the autocorrelation function $q(t)$ on a log-log plot for different values of p, as listed in the inset. The solid lines correspond to stretched exponential fits, with $\beta(p)$ and $\tau(p)$ as indicated in Figure 3. The error bars correspond to an estimate of the uncertainty of the points due to limited sampling.

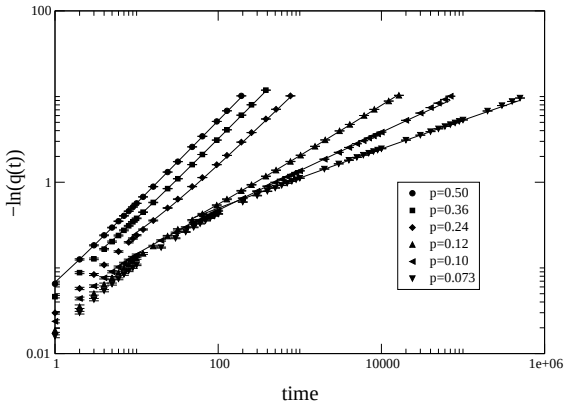

FIG. 2. A more stringent test of the stretched exponential behavior of $q(t)$ is the log [-log($q(t)$)] against log t plot. The different values of p are listed in the inset. The solid lines correspond to a stretched exponential fit, with β and τ as indicated in Figure 3

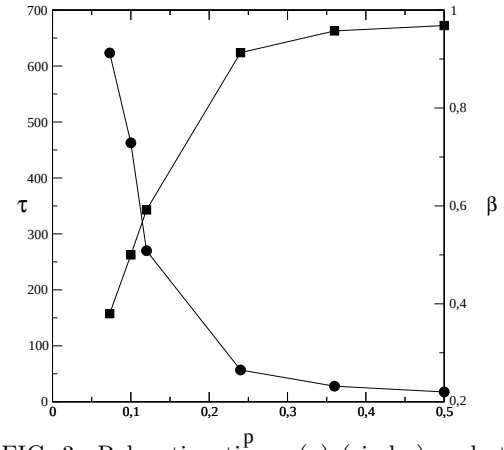

FIG. 3. Relaxation time $\tau(p)$ (circles) and stretched exponential exponent $\beta(p)$ (squares) against p. As $p \to p_c$, τ diverges while $\beta(p)$ approaches 1/3.

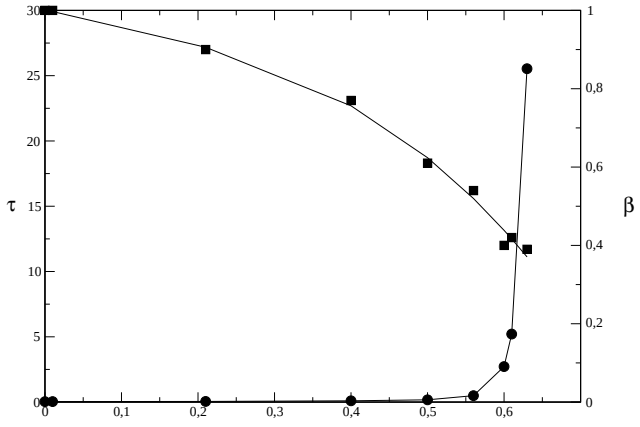

FIG. 4. Experimental data from light scattering measurements on a polystyrene colloid, taken from Bartsch et al ref [15]. In the publication the relaxation curves were parametrized using the KWW form. The relaxation was measured as a function of the colloid volume fraction ϕ. The critical value ϕ_c where a gel forms is about 0.69.